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UNITED STATES GOVERNMENT SPECIFICATION FOR
TITANIUM PIGMENT, DRY AND PASTE.

FEDERAL SPECIFICATIONS BOARD.

STANDARD SPECIFICATION No. 115.

This specification was officially adopted by the Federal Specifications Board on February 20, 1924, for the use of the Departments and Independent Establishments of the Government in the purchase of titanium pigment, dry and paste.

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1. GENERAL.

Titanium pigment may be ordered in the form of dry pigment or paste ground in linseed oil. The material shall be purchased by net weight.

(a) DRY PIGMENT.—The pigment shall be 25 per cent titanium oxide precipitated upon and coalesced with 75 per cent of blanc fixe (precipitated barium sulphate). It shall be thoroughly washed, shall be free from adulterants, and shall meet the following requirements.

Color—Color strength.—When specified, the color and color strength shall be equal to that of a sample mutually agreed upon by buyer and seller.

	Mini- mum.	Maxi- mum.
	Per cent.	Per cent.
Coarse particles retained on No. 325 sieve.....		1.0
Titanium oxide (TiO ₂).....	24.0	
Total impurities, including moisture.....		1.0
The remainder shall be barium sulphate.		

(b) PASTE.—The paste shall be made by thoroughly grinding the above-described pigment with pure, raw, or refined linseed oil.

The paste as received shall not be caked in the container and shall break up readily in oil to form a smooth paint of brushing consistency. The paste shall consist of:

	Mini- mum.	Maxi- mum.
	Per cent.	Per cent.
Pigment.....	80.0	85.0
Linseed oil.....	15.0	20.0
Moisture and other volatile matter.....		.7
Coarse particles and "skins" (total residue retained on No. 325 sieve, based on pigment).....		1.5

Deliveries will, in general, be sampled and tested by the following methods, but the purchaser reserves the right to use any additional available information to ascertain whether the material meets the specification.

2. SAMPLING.

It is mutually agreed by buyer and seller that a single package out of each lot of not more than 1,000 packages be taken as representative of the whole.

(a) DRY PIGMENT.—The package is to be opened by the inspector and a sample of not less than 5 pounds taken at random from the contents and sent to the laboratory for test.

(b) PASTE.—Whenever possible, an original unopened container shall be sent to the laboratory; and when this is for any reason not done the inspector shall determine by thoroughly testing with a paddle or spatula whether the material meets the requirement regarding not caking in the container. (See 4 (a).) After assuring himself that the paste is not caked in the can, the inspector shall draw a sample of not less than 5 pounds of the thoroughly mixed paste, place it in a clean, dry metal or glass container, which must be filled with the sample, closed with a tight cover, sealed, marked, and sent to the laboratory for test with the inspector's report on caking in container.

When requested, a duplicate sample may be taken from the same package and delivered to the seller, and the inspector may take a third sample to hold for test in case of dispute.

3. LABORATORY EXAMINATION, DRY PIGMENT.

(a) COLOR.—Take 5 g of the sample, add 1.5 cc of linseed oil, rub up on a stone slab or glass plate with a flat-bottomed glass or stone pestle or muller to a uniform smooth paste. Treat in a similar manner 5 g of the standard titanium pigment. Spread the two pastes side by side on a clear, colorless glass plate and compare the colors. If the sample is as white as or whiter than the "standard," it passes this test. If the "standard" is whiter than the sample, the material does not meet the specification.

(b) COLOR STRENGTH.—Weigh accurately 0.01 g of lampblack, place on a large glass plate or stone slab, add 0.2 cc of linseed oil and rub up with a flat-bottomed glass pestle or muller, then add exactly 10 g of the sample and 2.5 cc of linseed oil, and grind with a circular motion of the muller 50 times; gather up with a sharp-edged spatula and grind out twice more in a like manner, giving the pestle a uniform pressure. Treat another 0.01 g of lampblack in the same manner, except that 10 g of standard titanium pigment is used instead of 10 g of the sample. Spread the two pastes side by side on a glass microscope slide and compare the colors. If the sample is as light as or lighter in color than the "standard," it passes this test. If the "standard" is lighter in color than the sample, the material does not meet the specification.

(c) COARSE PARTICLES.¹—Dry in an oven at 105 to 110° C. a No. 325 sieve, cool, and weigh accurately. Weigh 10 g of the sample, wash with water through the sieve, breaking up all lumps either by gentle pressure with a pestle in a mortar, but not grinding, or with a brush on the sieve. After washing with water until all but the particles too coarse to pass the sieve have been washed through, dry the sieve for one hour at 105 to 110° C., cool, and weigh.

(d) QUALITATIVE ANALYSIS.—Place a small amount (about one-half gram) of the sample in a 250 cc Pyrex glass beaker; add 20 cc of concentrated sulphuric acid and 7 to 8 g of ammonium sulphate. Mix well, and boil for a few minutes. The sample should

¹ For a general discussion of sieve tests of pigments and data regarding many pigments on the market see Circular No. 148 of the Educational Bureau, scientific section, Paint Manufacturers' Association of the United States.

go completely into solution; a residue denotes the presence of silica or siliceous matter. Cool the solution, dilute with 100 cc of water, heat to boiling, settle, filter, wash with hot 5 per cent sulphuric acid until free from titanium, and test the residue for lead, etc. Test the filtrate for calcium, zinc, iron, chromium, etc., by regular methods of qualitative analysis. For the iron determination take a portion of the filtrate, add 5 g of tartaric acid, make slightly ammoniacal, pass in hydrogen sulphide in excess, and digest at the side of a steam bath for a while. No precipitate denotes absence of iron, nickel, cobalt, lead, copper, etc. A black precipitate easily soluble in dilute hydrochloric acid denotes iron. For titanium test a small portion of the original filtrate with hydrogen peroxide (a clear yellow-orange color should result) and another portion with metallic tin or zinc (a pale blue to violet coloration should result).

The pigment should show negative tests for sulphide sulphur, carbonates, and appreciable water-soluble matter.

(e) **MOISTURE.**—Place 1 g of the sample in a wide-mouth, short weighing tube provided with a glass stopper. Heat with the stopper removed for two hours at a temperature between 105 and 110° C. Insert the stopper, cool, and weigh. Calculate the loss in weight as moisture.

(f) **MATTER SOLUBLE IN WATER.**—Transfer 2.5 g of the pigment to a graduated 250 cc flask, add 100 cc of water, boil for five minutes, cool, fill to the mark with water, mix, and allow to settle. Pour the supernatant liquid through a dry filter paper and discard the first 20 cc. Then evaporate 100 cc of the clear filtrate to dryness in a weighed dish, heat for one hour at 105 to 110° C., cool, and weigh.

(g) **TITANIUM OXIDE.**—Transfer 0.5 g of the dried sample to a 250 cc Pyrex beaker, add 20 cc of concentrated sulphuric acid and 7 to 8 g of ammonium sulphate. Mix well and heat on a hot plate until fumes of sulphuric acid are evolved, and then continue the heating over a strong flame until solution is complete (usually not over five minutes of boiling) or it is apparent that the residue is composed of silica or siliceous matter. Caution should be observed in visually examining this hot solution. Cool the solution, dilute with 100 cc of water, stir, heat carefully to boiling while stirring, settle, filter through paper and transfer the precipitate completely to the paper. Wash the insoluble residue with cold 5 per cent (by volume) sulphuric acid until titanium is removed.

Dilute the filtrate to 200 cc and add about 10 cc of ammonia, specific gravity 0.90, to lower the acidity to approximately 5 per cent sulphuric acid (by volume).

Wash out a Jones reductor² with dilute 5 per cent (by volume) sulphuric acid and water, leaving sufficient water in the reductor to fill to the upper level of the zinc. (These washings should require not more than one or two drops of 0.1 *N* potassium permanganate solution to obtain the pink color.) Empty the receiver, and put in it 25 cc (measured in a graduate) of ferric sulphate solution. (See Reagents.) Reduce the prepared titanium solution as follows: (1) Run 50 cc of the 5 per cent sulphuric acid solution through the reductor at a speed of about 100 cc per minute; (2) follow this with the titanium solution; (3) wash out with 100 cc of 5 per cent sulphuric acid; (4) finally run through about 100 cc of water.

Care should be observed that the reductor is always filled with solution or water to the upper level of the zinc.

Gradually release the suction, wash thoroughly the glass tube that was immersed in the ferric sulphate solution, remove the receiver, and titrate immediately with 0.1 *N* potassium permanganate solution. (See Reagents.)

$$\begin{aligned} 1 \text{ cc } 0.1 \text{ } N \text{ KMnO}_4 &= 0.00481 \text{ g Ti} \\ &= 0.00801 \text{ g TiO}_2 \end{aligned}$$

Run a blank determination, using the same reagents, washing the reductor as in the above determination. Subtract this permanganate reading from the original reading and calculate the final reading to titanium dioxide (TiO₂) (which will include iron, chromium, arsenic, and any other substance which is reduced by zinc and acid). (See 3 (i) for reporting TiO₂.)³

(h) DETERMINATION OF BARIUM SULPHATE.—Ignite and weigh the precipitate of BaSO₄ obtained in separating the titanium.⁴ (See 3 (g).)

(i) IRON OXIDE.—Prepare a standard ferric solution containing 0.00001 g Fe per cc. (See Reagents.) Weigh a 1 g portion of the sample and treat as in 3 (g), transfer without filtering to a 200 cc flask, cool, fill to the mark, and determine iron colorimetrically in 50 cc aliquots in the following manner. Filter through a

² Directions for preparing a Jones reductor may be found in Blair, "The Chemical Analysis of Iron," 8th ed. Lippincott & Co., or Treadwell-Hall, "Analytical Chemistry," 5th ed. J. Wiley & Sons, p. 638.

³ Any other accurate method of determining titanium oxide may be used. For a discussion of various methods see "The Analysis of Silicate and Carbonate Rocks," by W. F. Hillebrand, U. S. Geological Survey Bulletin 700.

⁴ If the sample is impure it may be necessary to purify this precipitate, using appropriate methods.

dry filter paper (discarding the first 20 cc), and transfer 50 cc of the filtrate to a clean 100 cc Nessler tube or other color comparator. Add a drop or two of 0.1 *N* KMnO_4 solution, to oxidize any ferrous iron until a faint pink color is obtained. Add 10 cc of ammonium or potassium thiocyanate solution (see Reagents), dilute to 100 cc, and mix thoroughly. Compare the color immediately with a series of standards, prepared side by side with the sample in similar tubes.

Prepare the standards from the standard ferric solution so as to have a range of from 0.000005 g Fe to 0.00004 g (0.5 to 4.0 cc). Dilute these amounts with distilled water to about 50 cc. Add just enough 0.1 *N* KMnO_4 to produce a faint pink and then 10 cc of the thiocyanate solution. Finally dilute all standards to 100 cc.

For a single sample it is more convenient to run the standard Fe solution from a burette into a Nessler tube containing the acid, 10 cc of the thiocyanate solution, and 60 to 70 cc of distilled water until the depth of the color thus produced on dilution to 100 cc and mixed exactly matches the sample. From the burette reading calculate the amount of Fe. The color comparisons must be made immediately after the standards are prepared.

Calculate the total iron found to Fe_2O_3 and report as such. Calculate the TiO_2 equivalent by multiplying by the factor 1.003 and subtract this figure from the total titanium oxide as determined in 3 (g) and report the remainder as TiO_2 .

4. LABORATORY EXAMINATION, PASTE.

(a) **CAKING IN CONTAINER.**—When an original package is received in the laboratory it shall be weighed, opened, and stirred with a stiff spatula or paddle. The paste must be no more difficult to break up and show no more caking than a normal good grade of titanium pigment paste. The paste shall finally be thoroughly mixed, removed from the container, the container wiped clean, and weighed. This weight subtracted from the weight of the original package gives the net weight of the contents. A portion of the thoroughly mixed paste shall be placed in a clean container, and the portions for the remaining tests promptly weighed out.

(b) **MIXING WITH LINSEED OIL.**—One hundred grams of the paste shall be placed in a cup, 40 cc of linseed oil added slowly with careful stirring and mixing with a spatula or paddle. The resulting mixture must be smooth and of good brushing consistency. Flow a portion of this paint on a clean glass plate. Let stand in a nearly vertical position at room temperature (65 to 100° F.).

The film after four hours shall show no streaking or separation within a distance of 4 inches from the top.

(c) **MOISTURE AND OTHER VOLATILE MATTER.**—Weigh accurately from 3 to 5 g of the paste into a tared flat-bottomed dish, about 5 cm in diameter, spreading the paste over the bottom. Heat at 105 to 110° C. for one hour, cool, and weigh. Calculate the loss in weight as the percentage of moisture and other volatile matter.

(d) **PERCENTAGE OF PIGMENT.**—Weigh accurately about 15 g of the paste into a weighed centrifuge tube. Add 20 to 30 cc of "extraction mixture" (see Reagents), mix thoroughly with a glass rod, wash the rod with more of the extraction mixture, and add sufficient of the reagent to make a total of 60 cc in the tube. Place the tube in the container of a centrifuge, surround with water, and counterbalance the container of the opposite arm with a similar tube or a tube with water. Whirl at a moderate speed until clear. Decant the clear supernatant liquid. Repeat the extraction twice with 40 cc portions of extraction mixture, and once with 40 cc of ether. After drawing off the ether, set the tube in a beaker of water at about 80° C. or on top of a warm oven for 10 minutes, then in an oven at 110 to 115° C. for two hours. Cool, weigh, and calculate the percentage of pigment.

(e) **EXAMINATION OF PIGMENT.**—Grind the pigment from (d) to a fine powder, pass through a No. 80 sieve to remove any "skins," and preserve in a stoppered tube and apply tests 3 (d), (f), (g), (h), and (i). If required, apply tests 3 (a) and (b) in comparison with a portion of pigment extracted from the standard paste in exactly the same manner as in extracting the sample.

(f) **PREPARATION OF FATTY ACIDS.**—To about 25 g of the paste in a porcelain casserole add 15 cc of aqueous sodium hydroxide (see Reagents), and 75 cc of ethyl alcohol, mix and heat uncovered on a steam bath until saponification is complete (about one hour). Add 100 cc of water, boil, add sulphuric acid of specific gravity 1.2 (8 to 10 cc in excess), boil, stir, and transfer to a separatory funnel to which some water has been previously added. Draw off as much as possible of the acid aqueous layer, wash once with water; then add 50 cc of water and 50 cc of ether. Shake very gently with a whirling motion to dissolve the fatty acids in the ether, but not violently, so as to avoid forming an emulsion. Draw off the aqueous layer and wash the ether layer with one 15 cc portion of water and then with 5 cc portions of water until free from sulphuric acid. Then draw off completely the water layer.

Transfer the ether solution to a dry flask, and add 25 to 50 g of anhydrous sodium sulphate. Stopper the flask and let stand with occasional skaking at a temperature below 25° C. until the water is completely removed from the ether solution, which will be shown by the solution becoming perfectly clear above the solid sodium sulphate. Decant this clear solution (if necessary through a dry filter paper) into a dry 100 cc Erlenmeyer flask. Pass a rapid current of dry air (pass through a CaCl_2 tower) into the mouth of the Erlenmeyer flask and heat to a temperature below 75° C. on a dry hot plate until the ether is entirely driven off.

It is important to follow all of the details, since ether generally contains alcohol, and after washing with water always contains water. It is very difficult to remove water and alcohol from fatty acids by evaporation, but the washing of the ether solution and subsequent drying with anhydrous sodium sulphate removes both water and alcohol. Ether, in the absence of water and alcohol, is easily removed from fatty acids by gentle heat.

The fatty acids prepared as above should be kept in a stoppered flask and examined at once.

(g) TEST FOR MINERAL OIL AND OTHER UNSAPONIFIABLE MATTER.—Place 10 drops of the fatty acid (f) in a 50 cc test tube, add 5 cc of alcoholic soda (see Reagents), boil vigorously for five minutes, add 40 cc of water, and mix; a clear solution indicates that not more than traces of unsaponifiable matter are present. If the solution is not clear, the oil is not pure linseed oil.

(h) IODINE NUMBER OF FATTY ACIDS.—Place a small quantity of the fatty acids (f) in a small weighing burette or beaker. Weigh accurately. Transfer (by dropping) about 0.15 g (0.10 to 0.20 g) to a 500 cc bottle having a well-ground glass stopper, or an Erlenmeyer flask having a specially flanged neck for the iodine test. Reweigh the burette or beaker and determine the amount of sample used. Add 10 cc of chloroform. Whirl the bottle to dissolve the sample. Add 10 cc of chloroform to two empty bottles like that used for the sample. Add to each bottle 25 cc of the Hanus solution (see Reagents) and let stand, with occasional shaking, for one-half hour. Add 10 cc of the 15 per cent potassium-iodide solution and 100 cc of water, and titrate with standard sodium thiosulphate, using starch as indicator. The titrations on the two blank tests should agree within 0.1 cc. From the iodine value of the thiosulphate solution and the difference between the average of the blank titrations and the titration on the sample, calculate the iodine number of the sample tested. (Iodine number

is centigrams of iodine to 1 g of sample.) If the iodine number is less than 170, the oil does not meet the specification.

(i) COARSE PARTICLES AND SKINS.—Dry in an oven at 105 to 110° C. a No. 325 sieve. Weigh an amount of paste containing 10 g of pigment (see 4 (d)), add 100 cc of kerosene, mix thoroughly, and wash with kerosene through the sieve, breaking up all lumps but not grinding. After washing with kerosene until all but particles too coarse to pass the sieve have been washed through, wash all kerosene from the sieve with ether or petroleum ether, heat the sieve for one hour at 105 to 110° C., cool, and weigh.

5. REAGENTS.

(a) EXTRACTION MIXTURE.—

10 volumes ether (ethyl ether).

6 volumes benzol.

4 volumes methyl alcohol.

1 volume acetone.

(b) AQUEOUS SODIUM HYDROXIDE.—Dissolve 100 g sodium hydroxide in distilled water and dilute to 300 cc.

(c) STANDARD SODIUM THIOSULPHATE SOLUTION.—Dissolve pure sodium thiosulphate in distilled water that has been well boiled to free it from carbon dioxide, in the proportion of 24.83 g of crystallized sodium thiosulphate to 1,000 cc of the solution. It is best to let this solution stand for about two weeks before standardizing. Standardize with pure resublimed iodine.⁵ This solution will be approximately decinormal, and it is best to leave it as it is after determining its exact iodine value rather than to attempt to adjust it to exactly decinormal. Preserve in a stock bottle provided with a guard tube filled with soda lime.

(d) STARCH SOLUTION.—Stir up 2 to 3 g of potato starch or 5 g of soluble starch with 100 cc of 1 per cent salicylic acid solution, add 300 to 400 cc of boiling water, and boil the mixture until the starch is practically dissolved, then dilute to 1 liter.

(e) POTASSIUM IODIDE SOLUTION.—Dissolve 150 g of potassium iodide free from iodate in distilled water, and dilute to 1,000 cc.

(f) HANUS SOLUTION.—Dissolve 13.2 g of iodine in 1,000 cc of 99.5 per cent glacial acetic acid which will not reduce chromic acid. Add enough bromine to double the halogen content, determined by titration (3 cc of bromine is about the proper

⁵ Treadwell-Hall, *Analytical Chemistry*, 2, 5th ed., p. 645.

amount). The iodine may be dissolved by the aid of heat, but the solution should be cold when the bromine is added.

(g) ALCOHOLIC SODIUM HYDROXIDE SOLUTION.—Dissolve pure sodium hydroxide in 95 per cent ethyl alcohol in the proportion of about 22 g per 1,000 cc. Let stand in a stoppered bottle. Decant the clear liquid into another bottle and keep well stoppered. This solution should be colorless or only slightly yellow when used, and it will keep colorless longer if the alcohol is previously treated with sodium hydroxide (about 80 g to 1,000 cc), kept at about 50° C. for 15 days and then distilled.

(h) 0.1 *N* POTASSIUM PERMANGANATE SOLUTION.—Dissolve 3.161 g of pure potassium permanganate in a liter of distilled water, let stand 8 to 14 days, siphon off the clear solution (or filter through an asbestos filter), and standardize as follows: In a 400 cc beaker dissolve 0.25 to 0.30 g of Bureau of Standards' sodium oxalate in 250 cc of hot water (80 to 90° C.) and add 15 cc of dilute sulphuric acid (1:1). Titrate at once with the potassium permanganate solution, *stirring the liquid vigorously and continuously*. The permanganate must not be added more rapidly than 10 to 15 cc per minute, and the last 0.5 to 1 cc must be added dropwise with particular care to allow each drop to be fully decolorized before the next is introduced. The solution should not be below 60° C. by the time the end point is reached. (More rapid cooling may be prevented by allowing the beaker to stand on a small asbestos-covered hot plate during the titration. The use of a small thermometer as a stirring rod is most convenient.) The weight of sodium oxalate used multiplied by 0.8334 gives its iron equivalent, or multiplied by 1.1954 gives its titanium dioxide (TiO₂) equivalent⁶. The permanganate solution should be kept in a glass-stoppered bottle painted black to keep out light.

(i) FERRIC SULPHATE SOLUTION FOR TITANIUM.—A solution containing 2 per cent of iron as ferric sulphate is desired and may be prepared as follows: Dissolve 20 g of pure iron or plain carbon steel in a slight excess of hydrochloric acid, oxidize with nitric acid, heat with about 80 cc of sulphuric acid until fumes are evolved, finally cool, and dilute to 1,000 cc, set on steam bath, until dissolved, and filter if necessary. Add 0.1 *N* permanganate solution until a faint pink color shows that any ferrous iron has been oxidized. Ferric ammonium sulphate may also be used⁷.

⁶ International Atomic Weights, 1921-22.

⁷ Gooch, *Methods in Chemical Analysis*, 1st ed., p. 426.

(j) STANDARD FERRIC SULPHATE SOLUTION FOR COLORIMETRIC DETERMINATION OF IRON.—Determine the strength of the ferric solution reagent used in 5 (i) in terms of iron and dilute this solution until one is obtained of the strength 1 cc = 0.00001 g Fe.

(k) POTASSIUM THIOCYANATE INDICATOR.—Prepare a 2 per cent solution of the pure salt in distilled water.

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